INDUSTRIAL WASTEWATER TREATMENT EMPLOYING SURFACE MODIFIED ACTIVATED CARBON

by

ZAHRINI IFFAH BINTI ABDUL KHALID

Dissertation submitted in partial fulfilment of

the requirements for the

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CERTIFICATION OF APPROVAL

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Approved by,

_____

(Dr Usama Mohamed Nour El Demerdash)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
July 2010

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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ZAHRINI IFFAH BINTI ABDUL KHALID

ABSTRACT

Wastewater need to be treated prior being discharge to the environment. The treated water can be reused and recycled to minimize the use of fresh make up water. There are a few stages involved in wastewater treatment and one of them is through adsorption using activated carbon. Activated carbon adsorbs the organic and inorganic pollutant remains in the water. After sometimes, the activated carbon will be saturated and need to be regenerated. By using activated carbon with high adsorptive capacity, the frequency of regeneration can be reduced. In fact, the amount needed can be lessen, therefore reducing the operating cost. The adsorption capacity can be increased by modifying the surface of activated carbon. Methods for modification will depend on the targeted impurities. This project is mainly focusing on the chemical modification using concentrated Potassium Hydroxide (KOH) solution. Based on the characterization analysis, the morphologies of the activated carbon changed after modification. There were more open pores and the surface area was higher. Adsorption study was conducted to see its effectiveness in adsorbing organic molecules, which is phenol. The equilibrium time for modified activated carbon was much lesser compared to the none modified. Besides that, a few parameters were manipulated to determine its optimum condition. pH 6 was the best pH for adsorption of phenol. Adsorbent dosage and initial phenol concentration was directly proportional to the percent of phenol uptake. The adsorption of phenol follows Langmuir isotherm with correlation more than 0.99. In conclusion, the modified activated carbon shows better performance in adsorbing phenol. The adsorptive capacity was increased from 2.45mg/g, to 5.05 mg/g.

ACKNOWLEDGMENT

First and foremost, I would like to express my praises to God for His blessing.

My deepest appreciation and gratitude is extended to my supervisor, Dr Usama Mohamed Nour El Demerdash for being very encouraging, supportive and responsive throughout the whole process of completing this final year project to fulfil the university requirement. Without his constant supervision and guidance, I may not be able to complete this project successfully.

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(ZAHRINI IFFAH BINTI ABDUL KHALID)

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ABBREVIATIONS

AC	:	Activated Carbon
BET	:	Brunauer-Emmett-Teller
BOD	:	Bio oxygen demand
COD	:	Chemical Oxygen Demand
FTIR	:	Fourier Transform Infrared
H_2SO_4	:	Sulphuric acid
KAC	:	Activated carbon modified with Potassium Hydroxide (KOH)
KOH	:	Potassium Hydroxide
NaOH	:	Sodium Hydroxide
PAC	:	Purified activated carbon
SEM	:	Scanning Electron Microscope
XRD	:	X-Ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Industrial wastewater treatment is the process of cleaning wastewater which was contaminated by industrial activities. Such process is very essential to ensure the contaminants in the wastewater do not exceed the permissible limit set by the government prior to discharge to the environment. Besides that, the treated water can be recycled and reused to reduce the use of fresh water, which is good for cost optimization.

Phenolic compound widely exists in the industrial effluent such as those from the oil refineries, leather, paint, pharmaceutical, and steel industries [1]. Due to its nature of being highly toxic, carcinogenic, and poor biodegradability, phenol concentration needs to be reduced as low as practicable, prior being discharged to the environment [2]. According to Malaysia's Environmental Quality Act, 1974, the limit of phenol concentration is 0.001mg/l for Standard A and 1.0mg/l for Standard B.

For removal of organic contaminant such as phenol, adsorption using activated carbon is the best method to be employed. Activated carbon is proven to be the most effective adsorbent due to its high efficiency in adsorbing organic and inorganic pollutants dissolved in water [3]. The adsorption capacity of activated carbon can be further enhanced through surface modification and the type of modification is depending on the target impurities [4].

Therefore, the present work aims at modifying the surface of commercial activated carbon by employing the chemical treatment method using Potassium Hydroxide (KOH). Subsequently, an adsorption study is conducted to compare the performance of the modified and non-modified activated carbon in adsorbing Phenol.

1.2 Problem Statement

Carbon adsorption is part of the process involved in the advanced (tertiary) treatment of industrial wastewater [5]. This process is highly necessary to remove the organic contaminant, which may cause resin fouling when it enters the ion exchange unit [6]. After undergo adsorption process for a period of time, the activated carbon need to be replaced, since it is concentrated with impurities. Instead of disposing the used activated carbon, it is being regenerated and reused for cost optimization [7]. However, the regeneration process requires some cost for it to be done. Therefore, less frequency of regeneration is mostly desired and it can be achieved by modifying the surface of activated carbon to increase its adsorption capacity.

Phenol is commonly traced in the industrial effluent and need to be removed from the wastewater due to its ability to cause harmful towards human health. For an effective phenol adsorption to occur, it is necessary to determine the optimum condition.

1.3 Objectives

The objectives of this project are:

1. To modify the surface of commercial activated carbon through chemical treatment using Potassium Hydroxide (KOH)
2. To compare the adsorption performance between unmodified and modified activated carbon in adsorbing Phenol.
3. To determine the optimum condition for adsorption of phenol.

1.4 Scope of study

This study is about enhancing the effectiveness of industrial wastewater treatment focusing on the adsorption process. Therefore, it is necessary to understand the stages in treating the wastewater and which part of the process involved adsorption. Industrial wastewater treatment is consisted of few stages which are pretreatment, primary treatment, secondary treatment, and advanced (tertiary) treatment [5].

The pretreatment is mainly to remove large materials from the wastewater that may hinder the following treatment. In the primary treatment, the light particles or suspended solid is settled down in a sedimentation tank.

The secondary treatment is about removal of soluble materials that require oxygen for decay, as well as further removal of suspended solids. The processes involved in this stage are trickling filters, activated sludge, and clarifier. The secondary stage can remove up to 85% the BOD, suspended solids, and all pathogen, yet tertiary treatment is still required to remove the remaining pollutant such as nitrogen, phosphorus, non-biological chemical oxygen demand (COD), and heavy metals [5].

There are a few processes in advanced wastewater treatment which are filtration, carbon adsorption, phosphorus removal and nitrogen removal. The carbon adsorption is highly effective to remove organics contaminant in wastewater. Removal of Nitrogen and Phosphorus are necessary to reduce the growth of algae.

This study is also focusing on the properties of activated carbon, and its application in wastewater treatment. Methods to modify its surface were identified, and the selection was made based on the targeted impurities. For this experiment, phenol was used as the pollutant. Details description of activated carbon is discussed further in Chapter 2.

After performing modification onto the surface of activated carbon, the adsorption study was conducted to see its effectiveness in adsorbing phenol. Therefore, deep understanding about adsorption process is highly necessary. The mechanism of adsorption process is further explained in section 2.3. Besides that, the operating condition for the adsorption process was manipulated to determine its optimum condition. The variables concerned were the pH, initial phenol concentration, and adsorbate dosage.

The surface analysis was done to compare the characteristic of activated carbon before and after the modification. The analyses involved were Scanning Electron Microscope (SEM), X-ray diffractometer (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). The functions of each analysis are described in Section 2.5. Besides that, the UV-vis Spectrophotometer was used to determine the initial and final concentration of phenol.

CHAPTER 2

LITERATURE REVIEW

2.1 Activated Carbon

Activated carbon is a crude form of graphite, except that it has a random imperfect structure which is highly porous over a broad range of pore sizes and visible cracks and crevices to molecular dimension [8]. There are three main forms of activated carbon which are granular activated carbon, powdered activated carbon, and pelleted activated carbon. However, this research is only focusing on the granular.

Activated carbon is manufactured from a variety of carbonaceous material such as coal, bituminous coal (lignite), bone, wood, and coconut shell. These base materials undergo carbonization process, where they are heated at high temperature, normally in the range of 400–700° C to drives out any volatiles [9, 10]. To activate the carbon, it is subjected to a second heat and steam treatment [9]. Activation occurs by heating the material to an elevated temperature, such as 800–900° C with steam or carbon dioxide to produce a carbon material having high porosity and a specific surface area that may be in excess of 1000 m^2/g [10].

Granular activated carbon adsorption has been used successfully for the advanced (tertiary) treatment of municipal and industrial wastewater. GAC is used to adsorb the relatively small quantities of soluble organic and inorganic compounds such as nitrogen, sulfides, and heavy metals remaining in the wastewater [7]. Table 1 shows the organic compounds amenable to be adsorbed by GAC.

Table 1: Organic Compound Adsorbed by GAC

Class	Example
Aromatic solvents	Benzene, toluene, xylene
Polynuclear aromatics	Naphthalene, biphenyl
Chlorinated aromatics	Chlorobenzene, PCBs, endrin, toxaphene, DDT
Phenolics	Phenol, cresol, resorcinol, nitrophenols, chlorophenols, alkyl phenols
Aromatic amines & high molecular weight aliphatic amines	Aniline, toluene diamine
Surfactants	Alkyl benzene sulfonates
Soluble organic dyes	Methylene blue, textiles, dyes
Fuels	Gasoline, kerosene, oil
Chlorinated solvents	Carbon tetrachloride, percholoroethylene
Aliphatic & aromatic acids	Tar acids, benzoic acids
Pesticides/herbicides	2,4-D, atrazine, simazine, aldicarb, alachlor, carbofuran

Source: United States Environmental Protection Agency 1984

2.2 Surface Modification

Although the effectiveness of activated carbon as an adsorbent for a wide range of pollutants is well known, more research on its modification is gaining prominence due to the need to develop enhanced affinity for specific contaminants and remove them from industrial and drinking water applications [3]. The attribute of the activated carbon such as the porosity, surface area, and surface functional group give significant impact towards the performance of activated carbon in adsorbing a specific contaminant [11]. These attributes can be changed through surface modification.

The surface chemistry of activated carbon is determined by the acidic and basic character of their surface, and can be changed by treating or impregnating them with oxidizing

agents either in gas phase or in aqueous solution [3]. Wenzhong and colleagues stated that the employment of oxidizing agent in wet or dry methods will generate three types of oxygen containing groups, which are acidic, basic, and neutral [11]. Each group has affinity towards different contaminant. The presence of acidic functional groups on AC enhances their metal adsorptive capacities but these functional groups are unfavorable for the adsorption of organics like phenolic compounds [12]. Therefore, it is essential to identify the target impurities prior performing the surface modification.

In general, the surface modification can be classified into three, which are chemical, physical, and biological modification. However, this study will focus on the chemical and thermal modification only. Figure 1 summarized the modification method.

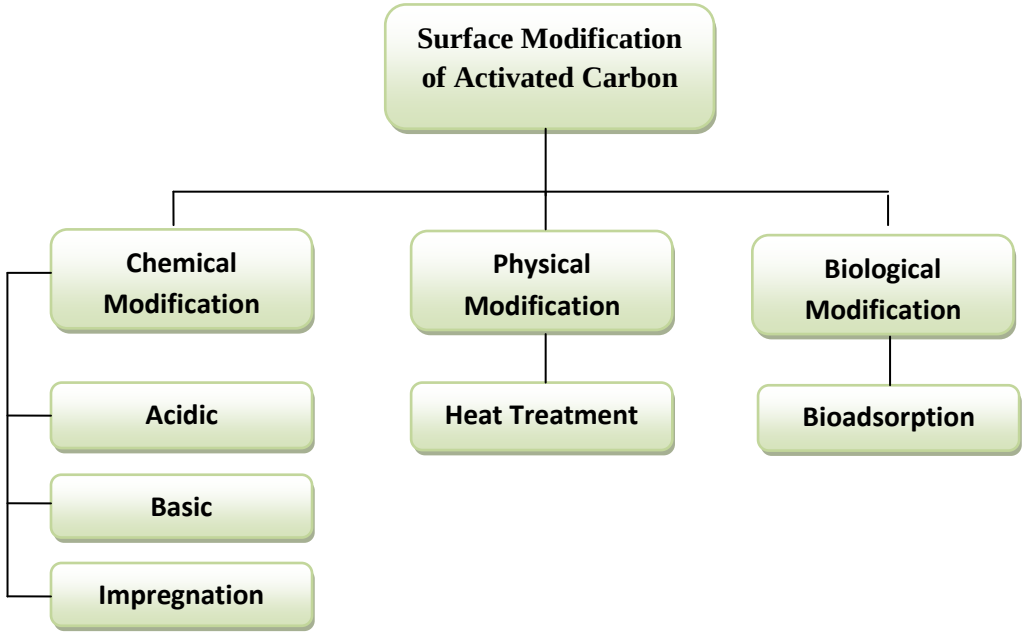


Figure 1: Surface modification method for Activated Carbon.

2.2.1 Chemical Modification

The chemical activation is carried out by impregnation of the activated carbon with acid, basic, or foreign metal, depending on the targeted impurities. Acidic treatment will form acidic surface functional group such as carboxyl, quinone, hydroxyl, carbonyl, carboxylic anhydride, and lactone, as shown in Figure 2 [11, 13]. These functional groups will increase the affinity towards metal ion, since metal ions have a tendency to form metal complexes with the negatively charged acid groups [12]. Figure 3 shows the cation exchange mechanism with the carbon surface carboxylic group. Besides that, the existence of acidic group will promote hydrophilicity on the carbon surface [14].

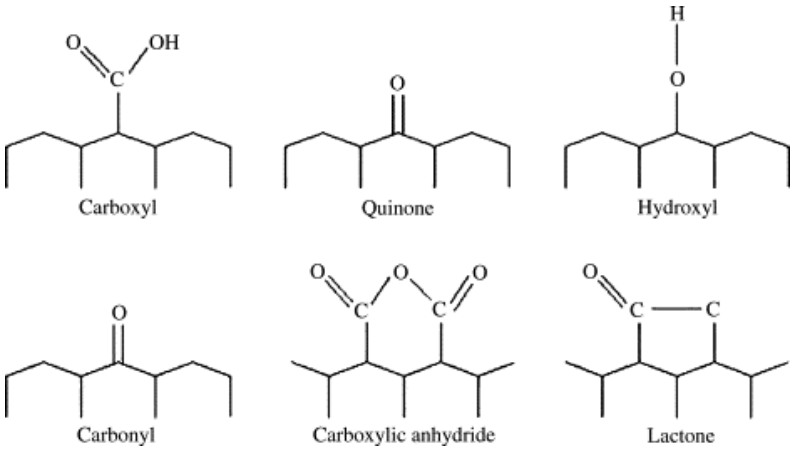


Figure 2: Some acidic surface groups bonded to aromatic rings on AC [11, 13]

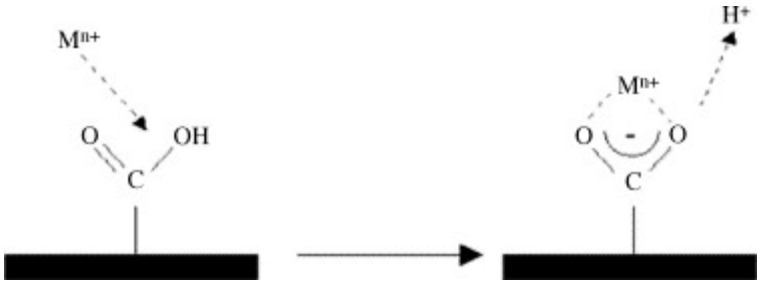


Figure 3: Cation exchange mechanism with the carbon surface carboxylic group [13]

Based on a study done by Chen, the maximum adsorption capacity for adsorption of copper increased from 6.14 mg Cu/g to 14.92 mg Cu/g after the activated carbon was treated with citric acid [15]. Edwin reported that the maximum adsorption capacity treated with nitric acid was enhanced from 0.5813 mg/g to 0.8881 mg/g [16]. Besides that, the adsorption of Cr (VI) is increased by factor of 1.7 when using activated carbon treated with hydrochloric acid [17]. However, acidic modification has disadvantages, where it will reduce the BET surface area and pore volume. This is due to the destruction of porous structures within AC during oxidation [12-15]. Besides that, acid modification does give adverse effect on the uptake of organics contaminant. The adsorption capacity of benzene onto activated treated with nitric acid is less than the non treated activated carbon [18].

As contrast to the acidic treatment, basic modification is highly favorable for adsorption of organic contaminant [18]. A research conducted by Yamin shows that the activated carbon treated with KOH demonstrate better performance in adsorbing organic dye of methylene blue [19]. Basic modification is commonly done by treating the activated carbon with aqueous ammonia and sodium hydroxide [12]. Through ammonization, the basic groups are formed on the surface such as C-H, C=N groups, amino, cyclic amides, nitrile group, ands pyrrole-like structure, as shown in Figure 4 [11]. Besides that, Chiang and friends reported that the activated carbon treated with sodium hydroxide shows increasing in phenolic group at its surface [20].

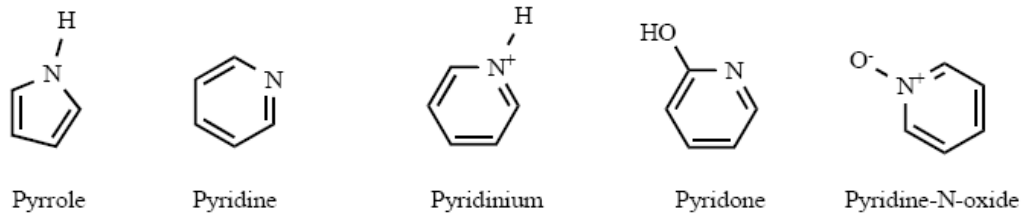


Figure 4: The Nitrogen functional forms possibly present in carbonaceous materials [11]

Surface impregnation is another modification method, where the impregnate does not have significant impact towards pH [13]. The term impregnation is defined as the fine distribution of chemicals and metal particles in the pores of AC [12]. The rational for employing impregnation are to optimize the catalytic properties of AC by promoting its built-in catalytic oxidation capability, to promote synergism between AC and the impregnating agent and to boost the capacity of AC as an inert porous carrier [12, 13]. Vivekanand reported that AC impregnated with silver, copper, nickel, aluminum and iron haveshown enhanced adsorption capacity and/or reactivity towards fluoride, cyanide and heavy metals like arsenic in water [12].

2.2.2 Physical Modification

Heat treatment is the major method reported for physical modification that partly remove some of the humic acids lodged in the micropores; therefore result in increase surface area [21]. Furthermore, the thermal treatment of activated carbon under inert flow is favorable for enhancing adsorption of organic compounds since the basic characteristic of activated carbon is amplified at high-temperature conditions [3, 11].

2.3 Adsorption

The process of adsorption involves separation of a substance, termed an adsorbate, from the liquid phase, and the concentration at the surface of a material termed an adsorbent [22]. The adsorption process takes place in four more or less definable steps which are bulk solution transport, film diffusion transport, pore transport, and adsorption. Figure 5 shows the definition sketch for the adsorption of an organic constituent with activated carbon [23].

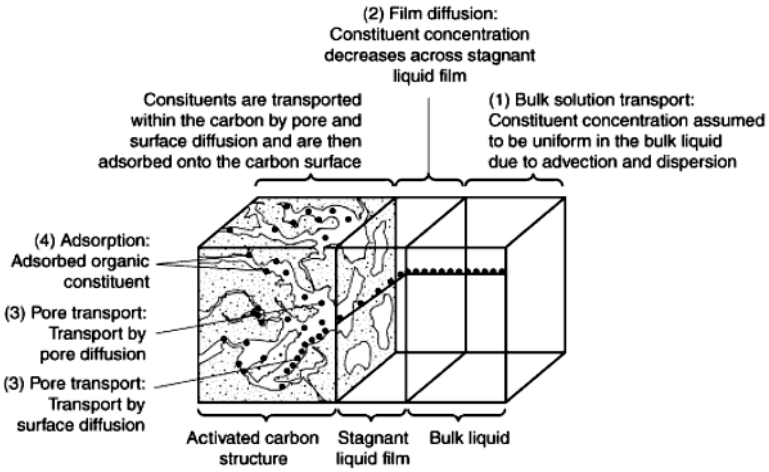


Figure 5: Definition sketch for adsorption of an organic constituent [23]

2.3.1 Adsorption Isotherm

Under standard conditions, the adsorptive capacity of activated carbon increases as the concentration increases until it a point of maximum saturation capacity [22]. At this stage, activated carbon needs to be replaced or reactivated. Isotherms are empirical relations, which are used to predict how much solute can be adsorbed by activated carbon. Adsorption isotherm is developed by exposing a given amount of adsorbate in a fixed volume of liquid to varying amounts of activated carbon [24]. There a few types of isotherm exist, but the most commonly use to describe adsorption characteristic of the activated carbon used in wastewater treatment is Freundlich Isotherm, defined as [22]:

$$\frac{x}{m} = K_f C_e^{1/n} \tag{1}$$

where x/m = mass of adsorbate adsorbed per unit mass of adsorbent,
mg adsorbate/g activated carbon

K_f = Freundlich capacity factor,
(mg adsorbate/g activated carbon)(L water/mg adsorbate) $^{1/n}$

C_e = equilibrium concentration of adsorbate in solution after adsorption, mg/L

1/n = Freundlich intensity parameter

The constants in the Freundlich isotherm can be determined by plotting log (x/m) versus log C_e and the Equation 1 is rewritten as [22]:

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n}\log C_e \qquad (2)$$

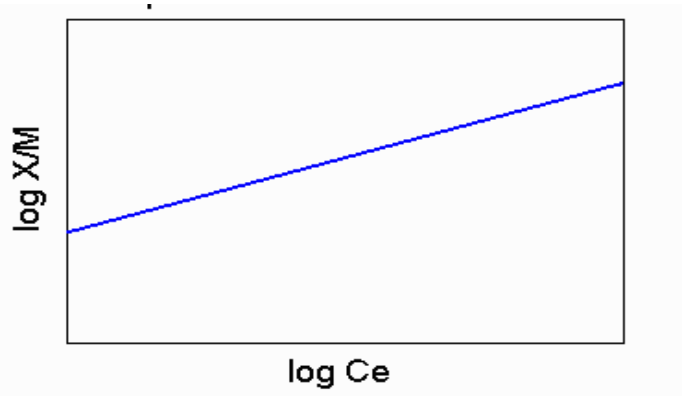


Figure 6: Freundlich Isotherm Curve

Another isotherm is called Langmuir Isotherm, which is defined as [22]:

$$\frac{x}{m} = \frac{abC_e}{1+bC_e} \qquad [3]$$

where x/m = mass of adsorbate adsorbed per unit mass of adsorbent, mg adsorbate/g activated carbon

a, b = empirical constant

C_e = equilibrium concentration of adsorbate in solution after adsorption, mg/L

The constants in the Langmuir isotherm can be determined by plotting C_e /(x/m) versus C_e and making use of Equation 3 rewritten as [22]:

$$\left(\frac{C_e}{(x/m)}\right) = \frac{1}{ab} + \frac{1}{a}C_e \tag{4}$$

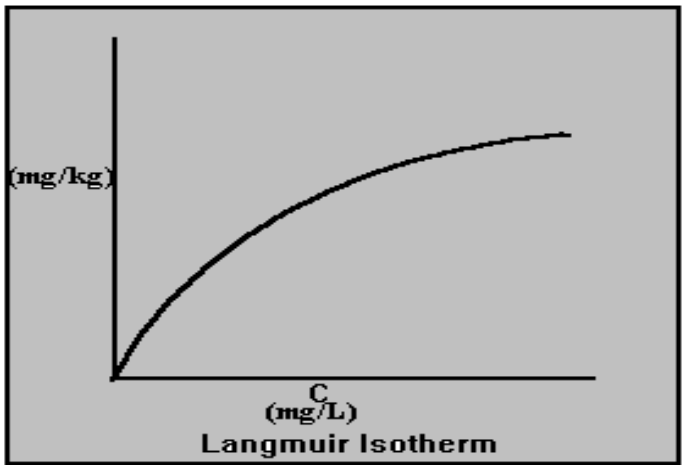


Figure 7: Langmuir Isotherm Curve

2.4 Adsorption of Phenol

Phenol is considered dangerous to people, since it may contribute to adverse effect of health. Therefore, it is necessary to remove this substance from wastewater. There are many methods that can be used to remove it, but the most effective way is through adsorption onto activated carbon. Based on an experiment done by Riaz, more than 98% of phenol was adsorb onto activated carbon [25].

There are a few factors that can influence the performance of adsorption such as pH, dosage of adsorbent, and adsorbate concentration. The adsorption of phenol at acidic pH does not give significant impact, except slightly increase with increasing pH. However, in the basic pH, the amount of phenol adsorbed decrease drastically [26]. Besides that, the dosage of activated carbon and adsorbate concentration is directly proportional to the adsorption of phenol onto activated carbon [25].

2.5 Characterization

2.5.1 Fourier Transform Infrared Spectrum (FTIR)

FTIR spectrum analysis was used to investigate variations in the functional groups of the sample. The increase and decreases in the spectrum peaks shows how the experimental conditions affect the structure of material. FTIR is used to identify chemicals that are either organic or inorganic.

2.5.2 X-ray Diffraction (XRD)

XRD is for the identification of crystalline compounds by their diffraction pattern.

2.5.3 Scanning Electron Microscope (SEM)

Conventional light microscopes use a series of glass lenses to bend light waves and create a magnified image. SEM creates the magnified images by using electrons instead of light waves. The SEM shows 3-dimensional images at much higher magnifications. The images are very detailed. The images created without light waves are rendered black and white. It can be used to estimate the pore size of the activated carbon quantitatively. Pore entrances, clearly visible as dark irregular shapes on lighter membrane background.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

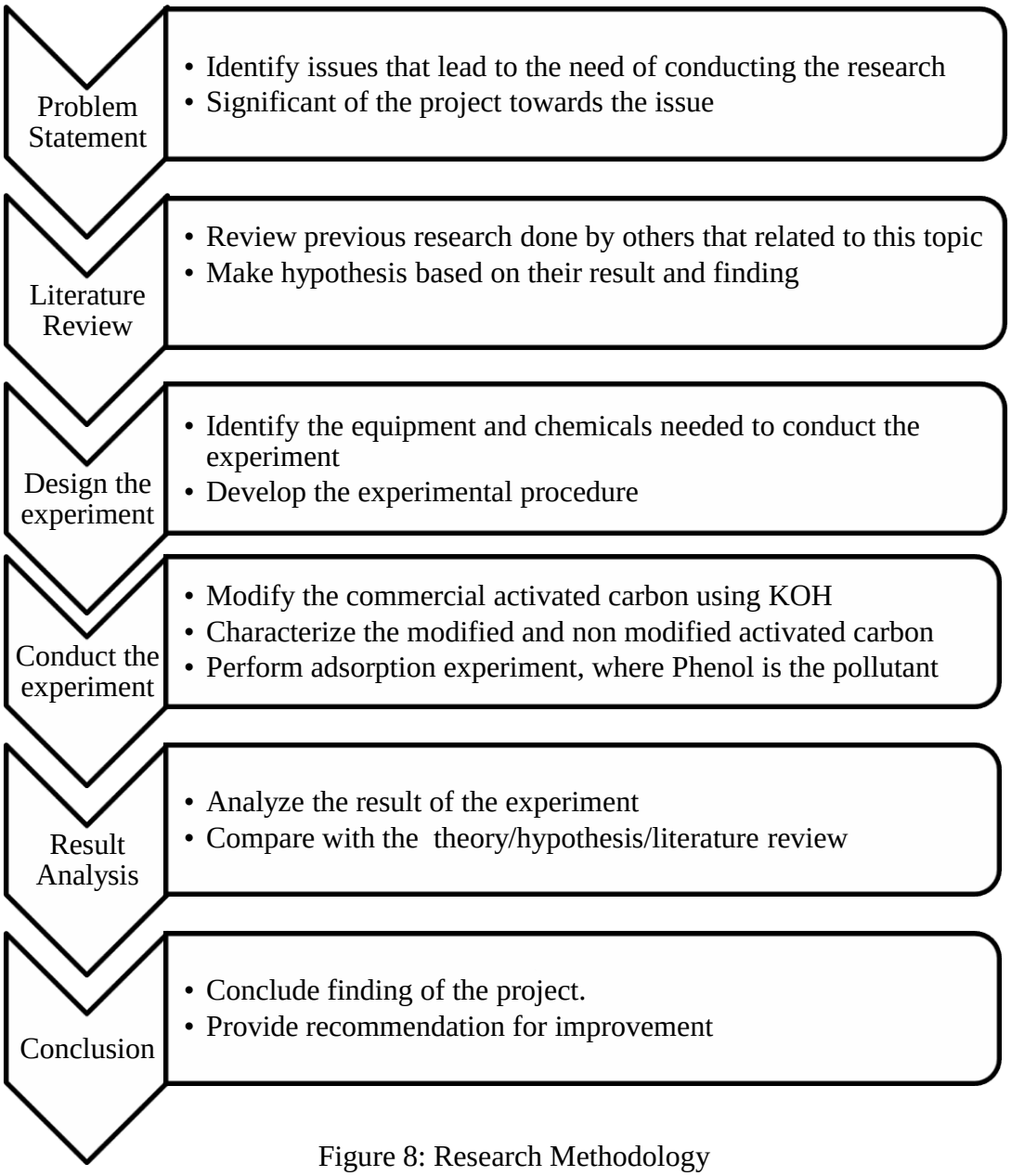


Figure 8: Research Methodology

3.2 Equipment and Chemicals

This experiment consists of two parts, where the first part is to prepare the modified activated carbon, and the second part is to conduct adsorption experiment using the modified and non modified activated carbon. Table 2 summarized the equipments and chemicals used in this project.

Table 2: List of equipments and chemicals

Equipment	Description
Fixed Bed Activated Unit	Used to activate the activated carbon after being treated with Potassium Hydroxide.
Oven (Mermaid)	Used to dry the activated carbon during modification process.
Water Bath Shaker (Italic Julabo water bath shaker)	Used for the adsorption experiment.
UV Vis Spectrophotometer (Shimadzu UV-3600)	Used to determine the initial and final concentration of phenol.
Chemicals	**Description**
Activated Carbon (Merck)	Adsorbent
Potassium Hydroxide (R&M)	Used to modify the activated carbon
Phenol (R&M)	Pollutant (Adsorbate)

3.3 Experimental Procedure

3.3.1 Materials

Commercial granular activated carbon (Merck) was used in this study. Prior to used, it was washed with distilled water to remove ash and subsequently dried using oven at 110^{o}C for 24 hours and noted as PAC. The adsorbate used was phenol, 92%.

3.3.2 Preparation of Modified Activated Carbon

The purified activated carbon was immersed in concentrated KOH solution (12M) for 24 hours, with stir. After completed, the resulting sample was repeatedly washed to neutralize the pH and remove any excess KOH. Subsequently, the sample was dried in oven for 24 hours at 110^{o}C. Then, the sample was placed in the Fixed Bed Activation Unit and heated from room temperature until 800^{o}C, under Nitrogen flow of 150cm^{3}/min. The sample was held at 800^{o}C for 3 hours before cooling to room temperature under Nitrogen flow. Once it reached room temperature, air is introduced. The sample is noted as KAC.

3.3.3 Characterization of Activated Carbon

All samples, the raw activated carbon, PAC, and KAC were sent for characterization using Fourier Transform Infrared Spectrum (FTIR), Scanning Electron Microscope (SEM), X-ray Diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FTIR).

3.3.4 Adsorption Studies

The adsorption of phenol on activated carbon was carried out using batch technique. The effect of contact time, solution pH, adsorbent dosage, and initial adsorbate concentration were investigated. For the effect of contact time, 50mL of 150ppm phenol was added into two different conical flask containing 0.2 g PAC and KAC and was shaken for 60minutes in water bath shaker at 25^{o}C with shaking grade 200rpm. The samples were withdrawn every 5 to 10 minutes time interval and the initial and final concentration were determined using UV-Vis spectrophotometer. The effect of contact time was used to determine the equilibrium time for the adsorption

For the effect of adsorbent dosage on phenol adsorption, various amount of adsorbent in the range of 0.1g to 0.6g were added to 250ppm phenol and was shaken until equilibrium. After shaking for 1 hour, the samples were taken and its final concentration was

determined using UV-Vis spectrophotometer. The experiment was done for both PAC and KAC

In the pH study, 0.2g of PAC and KAC were added into two different conical flasks containing 50mL of 150ppm phenol. The pH of phenol was adjusted to pH range 2 to 11 using NaOH and H_2SO_4.

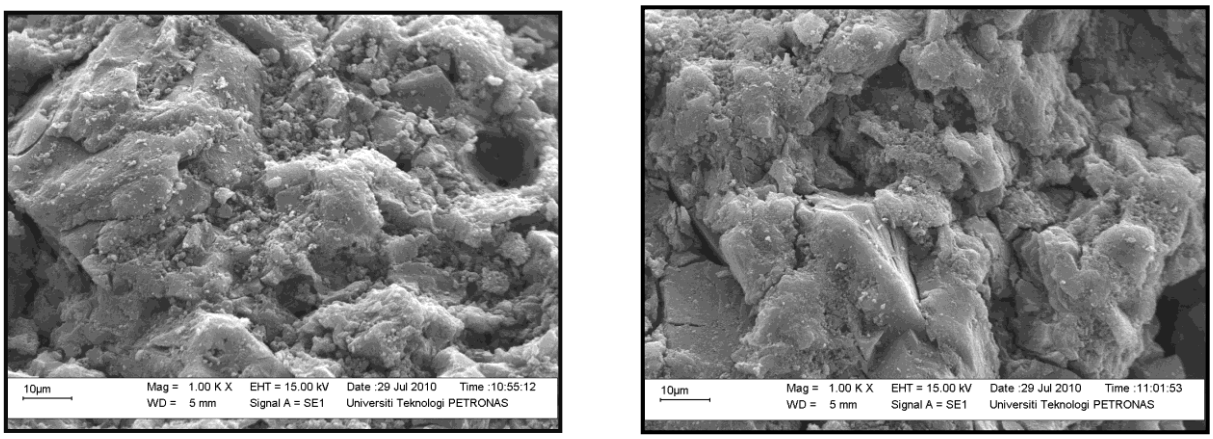
For the effect of adsorbate concentration, the adsorption was carried out using different phenol initial concentration ranging from 50ppm to 350ppm and same amount of adsorbent was used, which was 0.2g. This experiment was conducted for both PAC and KAC.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Characterization of Activated Carbon

4.1.1 Scanning Electron Microscope (SEM)



(a) (b)

Figure 9: SEM image for (a) PAC and (b) KAC

For adsorbent, the pore size distribution and surface area are the most important factors that will affect its performance in adsorbing the pollutant. The activation process is basically to produce a distribution of internal pores and enhance its adsorptive capacity. The pores of activated carbon are classified as macropores having an average diameter of greater than 50nm, mesopores with a diameter of 2-50nm, and micropores with a diameter less than 2nm. Figure 9 shows the SEM images for the activated carbon before and after undergoing the thermal and chemical modification using KOH. From the picture, we can observe that the physical and chemical activation, result in opening of pores on the surface of the activated carbon. The pores are irregular and different in sizes. The same result was also observed by Viboon and friends and they also mentioned that the macropores seems to be connected to mesopores [27]. Besides that, many research found that the thermal treatment improve the specific surface area and total pore volume of the activated carbon [29-31].

4.1.2 X-ray diffractometer (XRD)

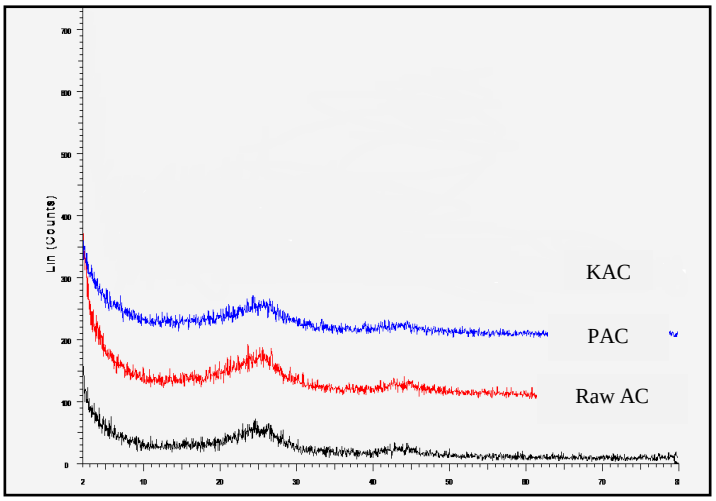


Figure 10: X-ray diffraction analysis

The crystal structure characteristics of the result samples are analyzed by x-ray diffractometer (XRD) as a radiation source. The measurement has been carried out in a scale 2θ and long duration scan 15s. The x-ray diffraction patterns of activated carbon sample are shown in Figure 10. At 2θ angle is 25^{o}C, there is indication of the presence of silica. Besides that, at angle 43^{o}C, it can be observed that there is graphitic basic plane on the activated carbon. Almost similar result was also obtained by Viboon *et al.* and their result is shown in Figure 11 [27]. It is observed that the result for all the raw, PAC, and KAC are almost similar.

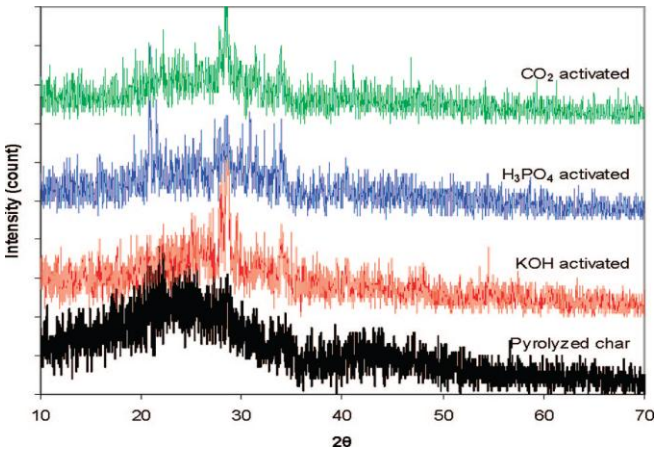
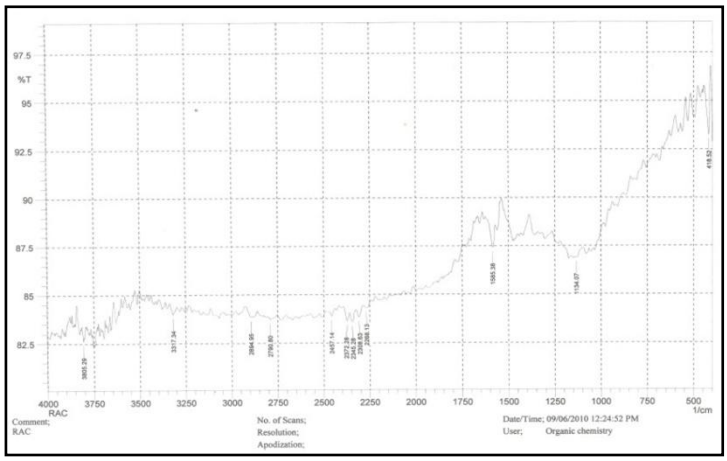
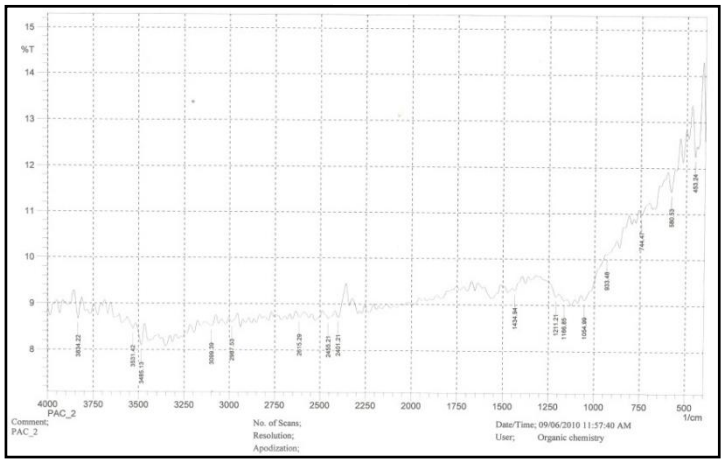


Figure 11: X-ray diffraction analysis [27]

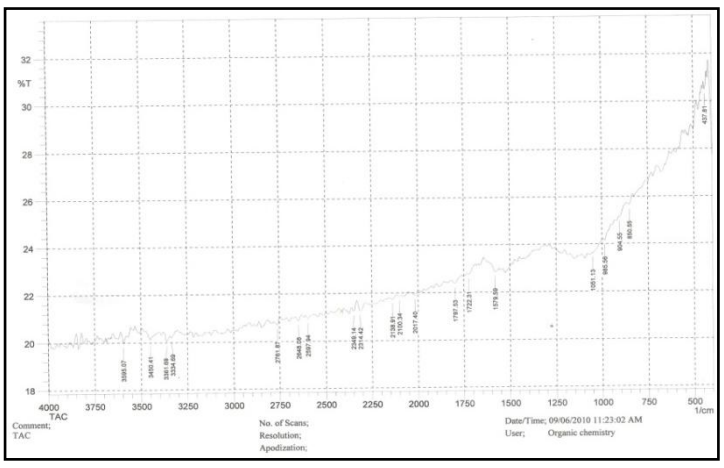
4.1.3 Fourier Transform-Infrared Spectroscopy (FTIR)



(a)



(b)



(c)

Figure 12: FTIR spectra for (a) Raw activated carbon, (b) PAC, and (c) KAC

A quantitative analysis of activated carbon was conducted by obtaining FTIR transmission spectra of the RAC, PAC, and KAC. The adsorption capacity of activated carbon depends upon porosity as well as the chemical reactivity of functional groups at the surface. Based on Figure 12, the FTIR spectra for all samples are almost similar. The stretching of –OH group is observed at wave number 3500 to 3640 cm^{-1}. However for KAC, such group was not observed. This might due to destruction of hydroxyl group (acidic surface group) during the thermal treatment at $800^{o}C$. Therefore, the activated carbons become more basic character and favorable for adsorption of organic molecules [11]. Besides that, after undergoing thermal treatment under Nitrogen flow, there are formation of new nitrogen-containing groups observed such as primary and secondary amine, which were observed at wave number 3400–3250 cm^{-1}. The peak at 3099.39cm^{-1} indicates there is stretching of alkenes group on the surface of activated carbon. The alkyl halide groups were also observed at wave number 1300 to 1150cm^{-1}

4.2 Adsorption Study

4.2.1 Effect of contact time

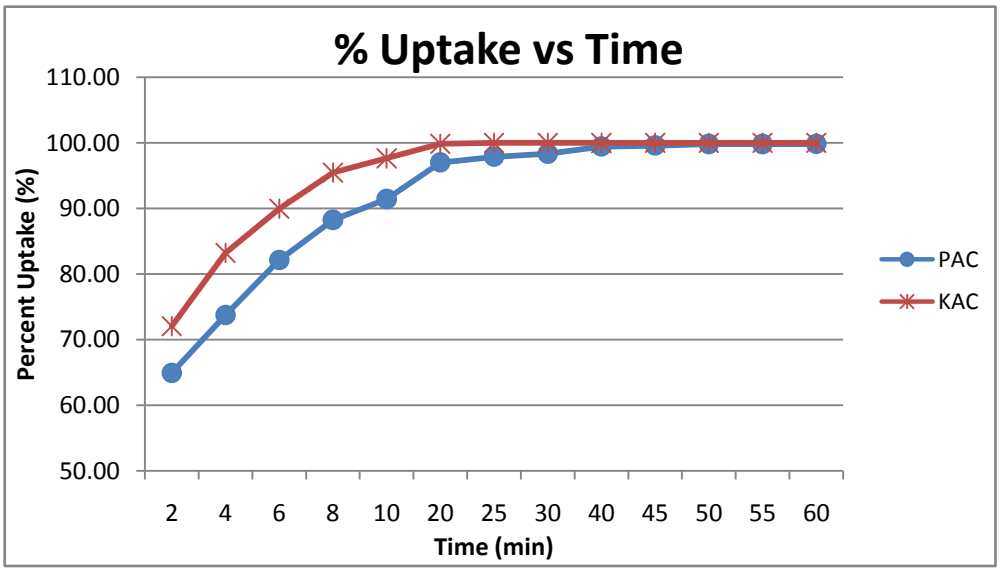


Figure 13: Effect of contact time on adsorption of phenol

Figure 13 shows the percent uptake of phenol after 1 hour. From this figure, it shows that the KAC starts to reach equilibrium at 20 min, while PAC at 30 min. This might due to greater surface area after the reactivation treatment of the activated carbon using KOH. Besides that, the change in the surface morphology of the activated carbon does lead to better adsorption of phenol. As illustrated in Figure 9(b), more pores were observed for the modified activated carbon.

This result is parallel to Yamin, where in his study the KOH modified activated carbon reached equilibrium earlier than the non modified activated carbon in adsorbing methylene blue [19]. Compared to research done by Riaz, the adsorption of phenol reach equilibrium at 5 minutes, which is much faster [25]. Besides that, Bestamin also reported in his study that phenol starts to saturate after 1 hour [28]. This deviation is might be due to the different type and amount of activated carbon used and different adsorbate concentration. High percentage of phenol uptake (>99%) indicates that activated carbon is very efficient in removing phenol from the aqueous solution.

4.2.2 Effect of pH

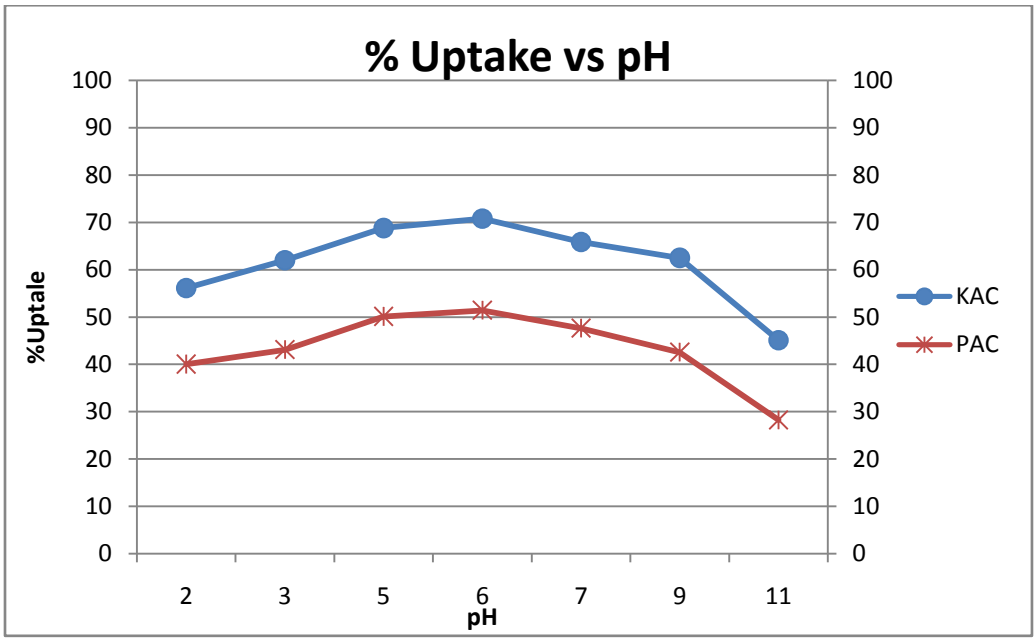


Figure 14: Effect of contact time on adsorption of phenol

The adsorption of phenol onto activated carbon is greatly influenced by the pH. The graph in Figure 14 shows that the uptake percentage of phenol at pH range 2 to 6 is increasing. After the optimum point, which is at pH 6, the pattern starts to decline. The same result was also observed by Sumol *et. al* in their experiment [32]. The effect of pH towards adsorption of phenol has the relationship with the adsorbent (activated carbon) pH_{ZPC} and the adsorbate (phenol) pKa. For phenol, the pKa is 9.89 [33]. The pH_{ZPC} of the activated was determined through experimental work and the result shows 5.2.

H_2SO_4 was used to adjust the pH to the acidic level. The introduction of anion SO_4^{2-} decrease phenol solubility [32]. This is because the anion has greater tendency to react with water molecules, compared to phenol. Decrease solubility means the relationship between adsorbate and adsorbent is weaken [32]. Therefore phenol tends to be adsorbed by the activated carbon. This explains the increasing of phenol uptake at lower pH.

The optimum pH for adsorption of phenol was observed to be at 6. This is because at pH lower than 6, the solutions is more acidic and there is a high enough H^+ concentration in the solution to cause the phenol to be protonated. The activated carbon is also positively charged, since pH< $pH_{ZPC.}$ Thus, this may cause extended repulsion [32]. On the other hand, at pH 6, where pH>$pH_{ZPC,}$ the activated carbon start to be negatively charged, therefore it have higher attraction to adsorb the protonated species [32-34].

At pH> pKa, (pH>9.89), there is a great tendency for phenol to dissociate and ionize into water-soluble phenolate anion, $C_6H_5O^-$. Hence, the solubility of phenol in water is increased and it tend to remain in the solution rather than been adsorbed onto the activated carbon [34]. This is why at high pH the percent uptake of phenol is reducing. The percent uptake of phenol using KAC is always higher than the PAC at every pH.

4.2.3 Effect of Adsorbent Dosage

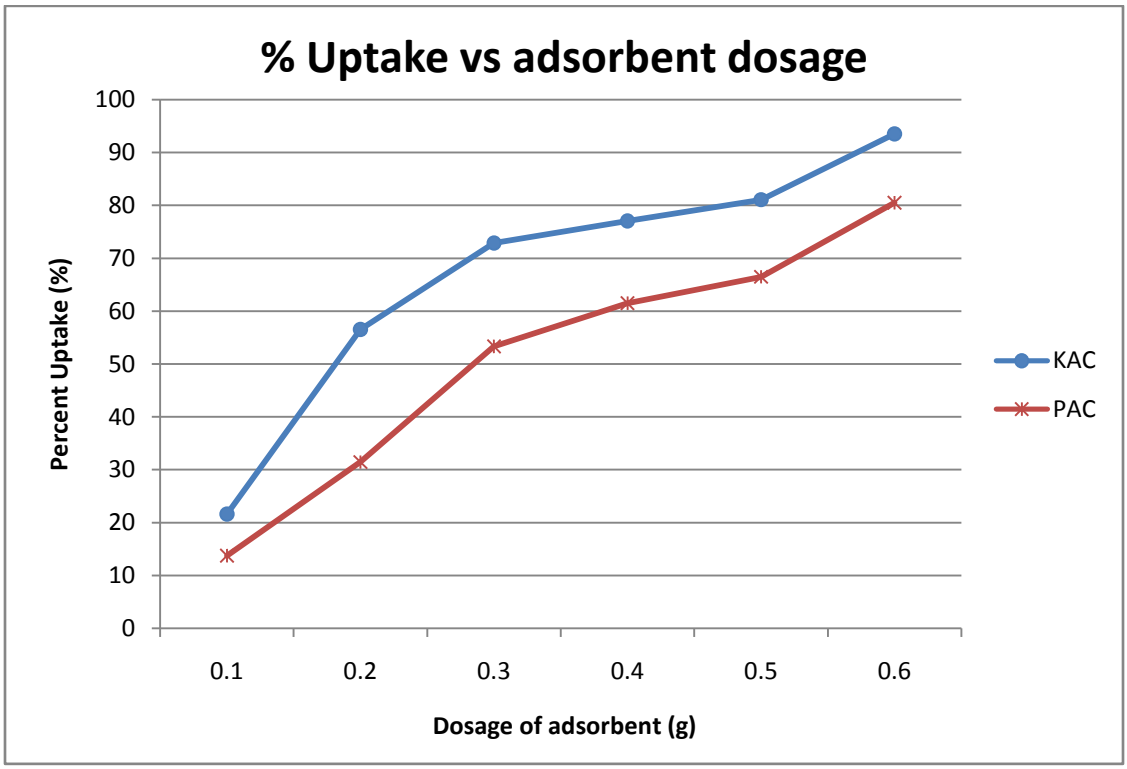


Figure 15: Effect of adsorbent dosage towards percent uptake of phenol

The adsorption of phenol is influenced by the adsorbent dosage. It determines the number of active surface area available for adsorption to occur [35]. To study the relationship, the amount of adsorbent used was varied from 0.1g to 0.6g. Figure 15 shows that the adsorbent dosage is directly proportional to the amount of phenol adsorb onto the activated carbon. The highest percent uptake was achieved when the most amount of adsorbent dosage used (0.6g). However, the increment is not in a linear manner. Such result is also observed by Saadet *et al.* in their experiment, removal of phenol on hexadecyl trimethyl ammonium-bentonite [36]. Besides that, Yamin also obtained similar result in his research adsorbing methylene blue using activated carbon [19]. Even thought different adsorbent and adsorbate were used, yet the pattern of the result is the same. By adding more adsorbent, it is actually increasing the site for adsorption to occur. Therefore, more phenol are adsorb onto the vacant area. Furthermore, the adsorbate and adsorbent interaction is becoming less hindered or less competition, contributes to easier adsorption.

4.2.4 Effect of Initial Concentration

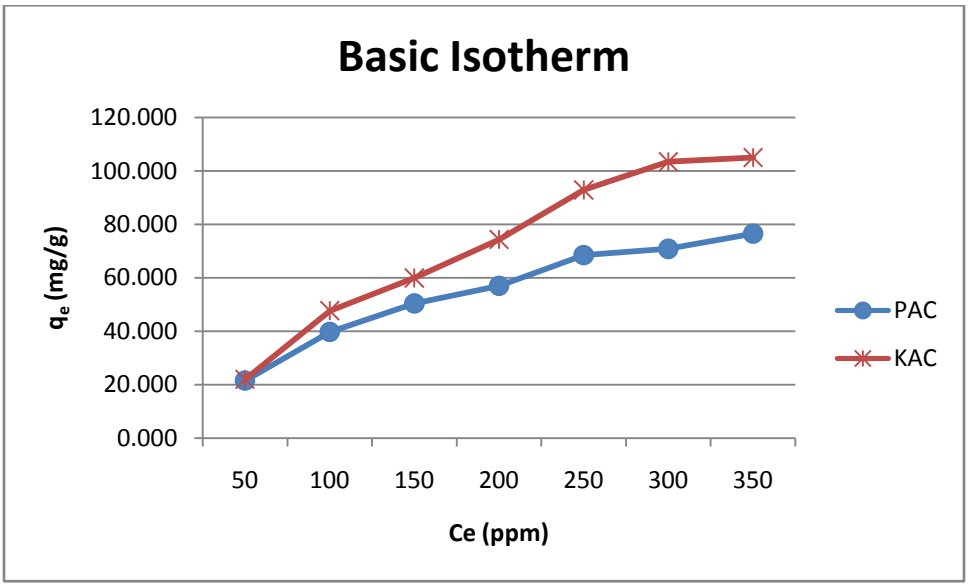


Figure 16: Adsorption isotherm

The adsorption isotherm was obtained as shown in Figure 16. The amount adsorbed on the activated carbon was determined using the relation [37]:

$$q_e = \frac{(C_o - C_e)V}{m} \tag{5}$$

where C_o and C_e is the initial and final concentration of phenol, V is the volume of aqueos solution, and m is the mass of activated carbon. In general, adsorption isotherm describes how much solute can be adsorbed by activated carbon. From the graph, it is clearly shown that as the initial concentration increase, the adsorptive capacity also increases. The same result was also achieved by Afshin *et al.* in their research on adsorption of carbolic acid (phenol) in aqueous solution [38]. They mentioned that the explanation for this is as the initial concentration increases, the mass transfer driving force is also increasing. Therefore, the rate at phenols molecule passes from the bulk solution is higher, leads to easier adsorption process to occur. However, the percentage uptake of phenol is decreasing, as the initial concentration increases. This might be due to the adsorbent is already saturated with phenol after being shaking for 1 hour. Therefore,

there are still a lot of phenol remain in the solution. Note that the percent uptake is calculated using the following equation [34]:

$$\%Uptake = \frac{C_{final} - C_{initial}}{C_{initial}} \times 100 \quad (6)$$

Hence, as the initial concentration increases, the percent uptake is decreases. The same result was also observed by Enamul *et. al* in their research, adsorption of phenol on mesoporous carbon [39]. The effect of initial concentration toward percent uptake is illustrated in Figure 17.

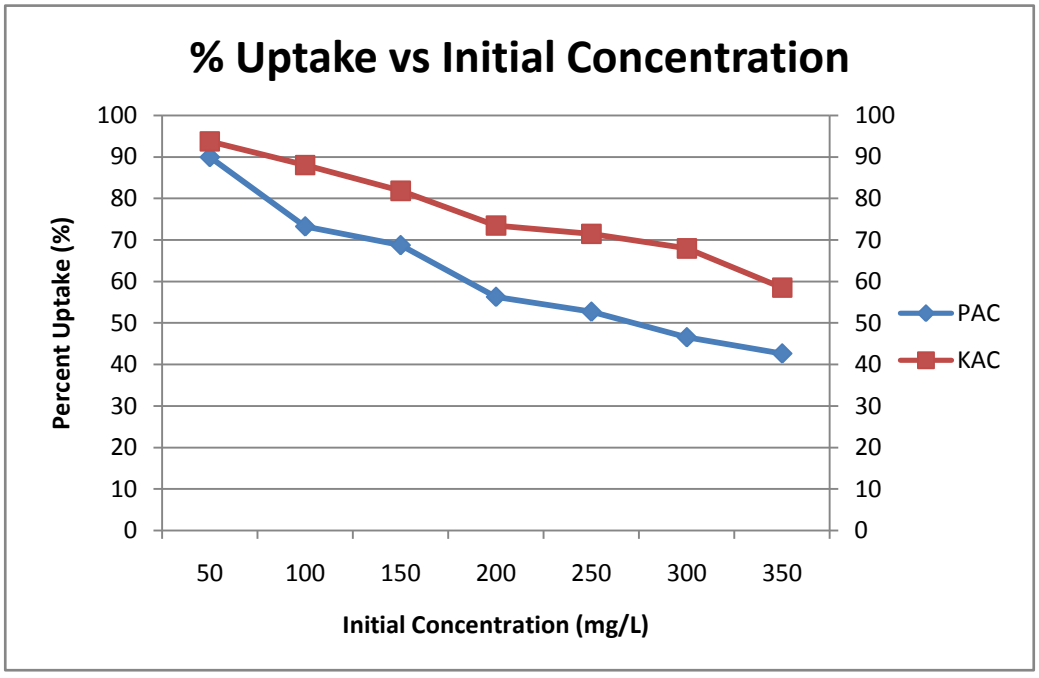


Figure 17: Effect of initial concentration towards percent uptake of phenol

Besides that, Langmuir isotherm is commonly used as a model to describe the adsorption isotherm. The Langmuir equation is given as [39]:

$$\left(\frac{C_e}{q_e}\right) = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e \qquad (7)$$

Where

C_e : equilibrium concentration of adsorbate (mg/L)

q_e : the amount of adsorbate adsorbed (mg/g)

Q_o : Langmuir constant (maximum adsorption capacity)

b : Langmuir constant (related to rate of adsorption)

The Langmuir constants can be determined from the graph. Figure 18 shows the Langmuir isothem graph for adsorption of phenol onto the modified and non-modified activated carbon.

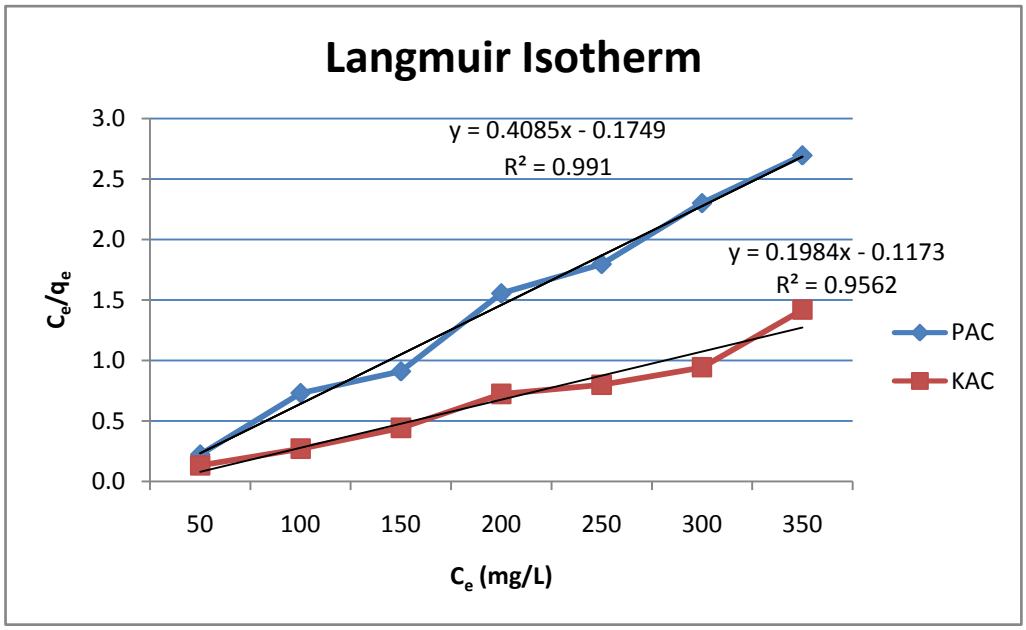


Figure 18: Langmuir isotherm for adsorption of phenol

The plot of C_e/q_e against C_e gives straight line for all concentration, implies that the adsorption is well fitted to Langmuir isotherm. The correlation for both PAC and KAC are 0.991 and 0.9562 respectively. Besides that, for PAC, the value of Q_o, which indicate the maximum adsorption capacity, is 2.45mg/g, while for KAC is 5.05 mg/g. This value once again proves that the adsorption capacity for KAC is higher compared to the PAC. This might due to higher surface area and more porosity after undergoing the KOH treatment.

CONCLUSION

The activated carbon modified with concentrated KOH shows better performance in adsorbing phenol. There is a change in the morphology of the activated carbon, where it becomes more pores and the surface area is higher. Besides that, from the adsorption study, it is proven that the adsorbent dosage is directly proportional to the percent uptake of phenol. The optimum pH for adsorption of phenol to occur is at pH6. The adsorption follows the Langmuir isotherm model with correlation > 0.99. Through the surface modification, the adsorption capacity of the activated carbon is increased about double of its original value (> 100%). Prior modification, the adsorption capacity is 2.45mg/g, and after the modification is 5.05 mg/g.

RECOMMENDATION

There are a few recommendations proposed to improve this project. The BET and porosity analysis shall be done for strong evidence about the increasing of surface area and porosity of activated carbon after the modification with concentrated KOH. Besides that, the effect of other parameters such as the concentration of KOH and activation temperature shall be investigated to determine the optimum condition for surface modification. There are also other methods used to modify the activated carbon such as through ammonization, and evaporation in concentrated solution. Perhaps, in the future, a comparison study on different method to modify the surface of activated carbon can be done. Finally, it is recommended to run the adsorption study using different pollutant, both the organic compound and heavy metal ion to confirm whether it is applicable to be used for other contaminants.

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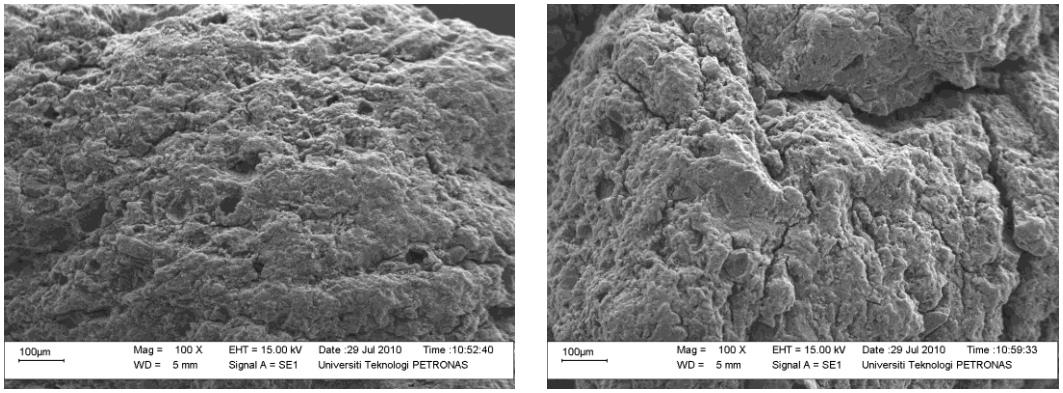
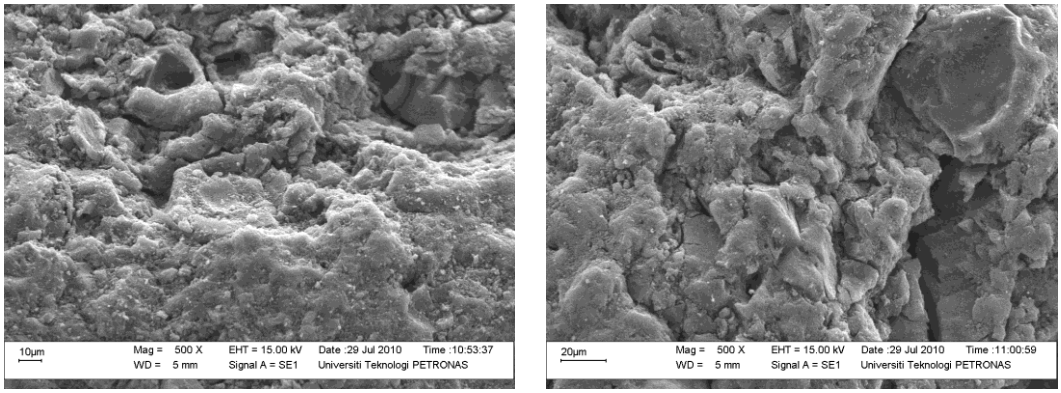
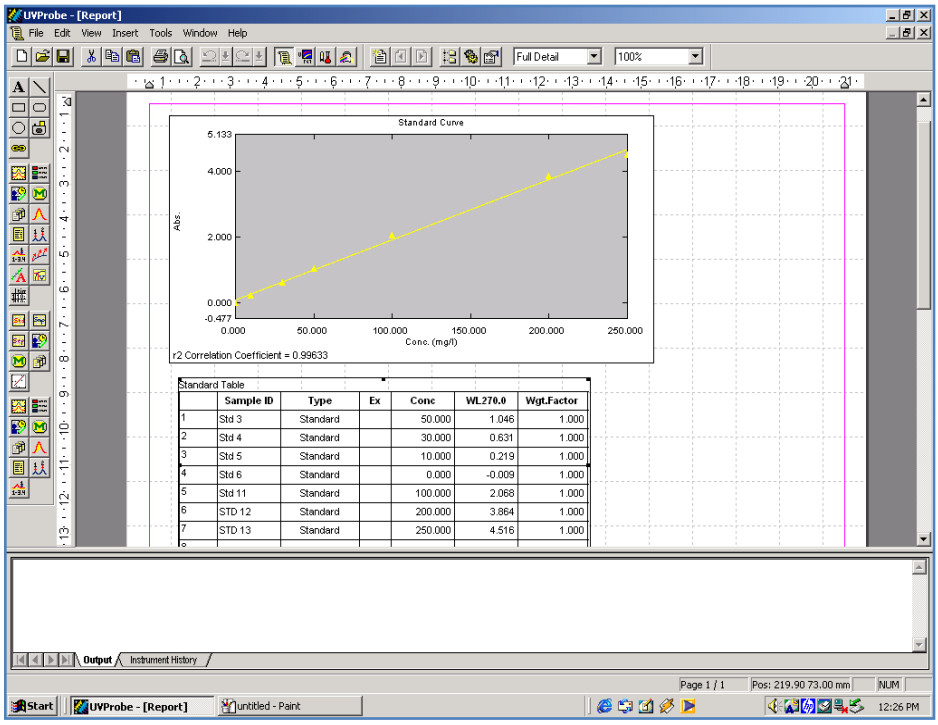
APPENDICES



SEM image at 100 magnifying**,** (a) PAC and (b) KAC



SEM image at 500 magnifying**,** (a) PAC and (b) KAC



Calibration curve of phenol, using UV-vis spectrophotometer

Fixed Bed activation unit